



Montmorillonite, vermiculite and saponite based porous clay heterostructures modified with transition metals as catalysts for the DeNOx process

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ABSTRACT

Porous clay heterostructures (PCHs) were synthesized from natural montmorillonite and vermiculite as well as synthetic saponite using the surfactant directed method. The direct synthesis of PCHs from saponite and montmorillonite was possible, while the pre-treatment of parent vermiculite with acids was necessary prior to the intercalation step. The PCH samples were characterized with respect to their composition (EPMA), structure (XRD, UV-vis-DRS), texture (BET), surface acidity (FT-IR) and chemical nature of the deposited transition metal species (UV-vis-DRS). Porous clay heterostructures as well as their derivatives modified by deposition of transition metal (Cu, Fe) oxides were tested as catalysts for the DeNOx process. The transition metal containing PCH samples were found to be active, selective and stable catalysts of this process. Their catalytic performance depended on the kind of the parent clay used for the PCH synthesis as well as deposited transition metals.

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1. Introduction

Porous clay heterostructures (PCHs) are a relatively new group of porous solids based on cationic layered clays. These composite materials consist of the clay layers separated by silica pillars. The synthesis of PCHs is presented in Scheme 1 and includes the following steps: (i) cationic templates and neutral amine co-templates are intercalated in the interlayer space of the host clay forming the micelle structures; (ii) the silica pillars are created by in-situ polymerization of a silica source around the micelle structures; (iii) the organic templates are removed from the material by calcination or extraction with suitable solvents, producing solid characterized by high surface area and porosity, high thermal and hydrothermal stability, significant surface acidity, ion-exchange properties, combined micro- and mesoporous structure. The properties of the PCH materials (e.g. surface acidity, CEC potential) depend on the type of the parent clay used for their synthesis. On the other hand the porous structure of the PCH materials can be controlled by selection of suitable surfactant and co-surfactant as well as synthesis conditions. Various types of cationic layered clays (fluorohectorite [1], montmorillonite [2],

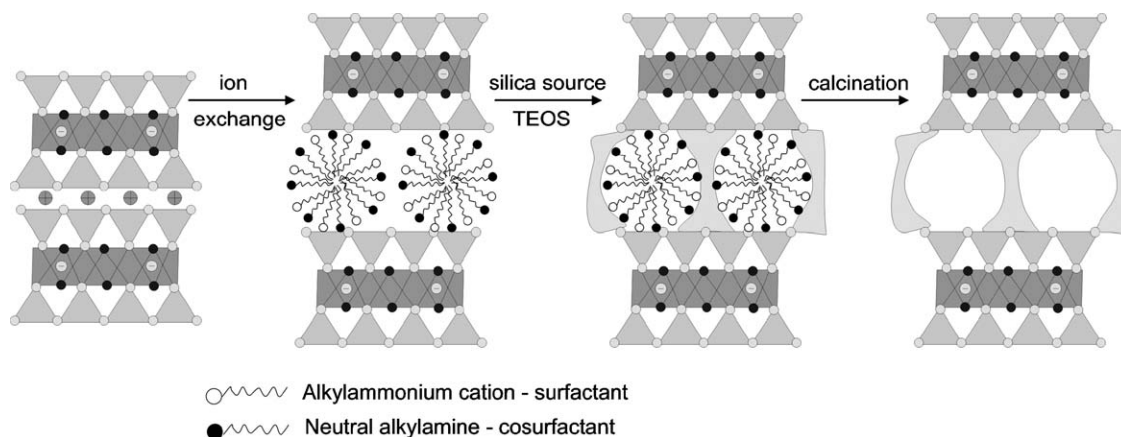
synthetic saponite [3], magadiite [4]) were used as precursor for the synthesis of the PCH materials. However, up till now, the synthesis of PCHs based on natural vermiculite has not been reported. The high potential of the interlayer cations stabilization in vermiculite strongly limits its ion-exchange properties and therefore, the deposition of cationic alkylammonium surfactants into the interlayer space of this clay is difficult or even impossible. Therefore, before the intercalation step, the charge of the vermiculite layers has to be reduced. The procedure of this operation was proposed by del Rey-Perez-Caballero and Poncelet [5]. In the first step Al^{3+} cations are partially leached from the tetrahedral sheets of vermiculite by treatment of the parent clay with a solution of nitric acid, while in the second step, aluminum cations deposited in the interlayer space of the clay are complexated by citric or oxalic acids and removed into solution. Such procedure was applied before conversion of vermiculite into the PCH material.

Porous clay heterostructures have been found to be very attractive materials for catalysis. Our previous studies focused on the PCH materials obtained from synthetic saponite have shown their very interesting catalytic properties in the selective reduction of NO with ammonia (DeNOx) [6] and selective catalytic oxidation of ammonia to nitrogen (NH_3 -SCO) [7].

The paper presents synthesis and characterization of PCHs obtained from various layered cationic clays (saponite,

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Scheme 1. Mechanism of cationic layered clays transformation into PCHs.

montmorillonite, vermiculite) as well as comparison of their catalytic performance in the DeNO_x process.

2. Experimental

2.1. Catalysts preparation

Synthetic saponite (Kunimine Industries Co., Japan) as well as natural montmorillonite and vermiculite (S&B Industrial Minerals GmbH, Greece) were used as starting materials for the PCH preparation. For the synthesis of PCHs from saponite and montmorillonite the procedure proposed by Benjelloun et al. [8] was applied. The sodium form of the parent clay (3 g) was added to a solution (0.1 M, 50 ml) of surfactant (hexadecyltrimethylammonium chloride) and stirred at 50 °C for 24 h. Subsequently, the clay was separated from the solution and washed with demineralised water till pH of 7 was reached. In the next step, 2 g of the modified clay was added to a neutral amine (dodecylamine) and a silica source (tetraethylorthosilicate – TEOS) in the following molar ratio: modified clay/dodecylamine/TEOS = 1/20/150. The mixture was allowed to react for 4 h under continuous stirring. Then the modified clay was separated from the solution, dried at room temperature and finally calcined. The PCH material based on saponite was calcined at 550 °C for 6 h, while the PCH sample obtained from montmorillonite was calcined at temperature 600 °C for 6 h.

The synthesis of the PCH materials from natural vermiculite was more complex. Vermiculites are characterized by significantly higher potential of the interlayer cations stabilization than montmorillonite and saponite. Therefore, their direct intercalation with surfactant molecules is very difficult or even impossible [5]. The stabilization potential of interlayer cations can be reduced by a partial leaching of Al³⁺ cations from the tetrahedral sheets of vermiculite by treatment of the parent clay in acidic medium. Part of leached aluminium ions is located in the interlayer space of the clay. These extraframework aluminium ions are removed into a solution using complexing acids. Then the modified clay can be converted into the sodium form by an ion exchange method. In the next step, such charge-reduced vermiculite can be easily transformed into the PCH-type materials.

Raw vermiculite was leached with nitric acid (solution of 0.8 M) at 95 °C for 8 h under stirring. The amount of acid corresponded to a mol H⁺/g clay ratio of 0.008. Then, the modified clay was washed, separated by filtration and oven dried at 120 °C for 12 h. In the next step, the acid treated clay sample was calcined at 600 °C for 4 h. Calcined vermiculite was washed with an oxalic acid solution

(0.2 M) at 80 °C for 3 h. The amount of oxalic acid corresponded to 1 g of the clay was 0.002 M. Then, the solid was washed, separated by filtration and oven dried (120 °C/12 h). Finally, modified vermiculite was transformed into a sodium form by an ion-exchange method with an aqueous solution (1 M) of NaCl at 95 °C under stirring. Then, the solid was washed and oven dried at 120 °C for 12 h. After such modification, the vermiculite sample was ready for the synthesis of the PCH-type material. The next steps of the synthesis were performed using the procedure applied for the modification of saponite and montmorillonite. Finally, the obtained PCH material was calcined at temperature 600 °C for 6 h.

Transition metals (Cu and Fe) were deposited on the PCH supports by an ion-exchange method using aqueous solutions (0.02 M) of Cu(NO₃)₂·H₂O or Fe(NO₃)₃·9H₂O. The slurry of 2 g of the PCH sample in 200 ml of nitrate solution was stirred at 60 °C for 3 h. Then, the solid was separated by filtration, washed and oven dried at 120 °C for 12 h. The samples modified with copper and iron were dried at room temperature and then calcined in the air atmosphere at 450 °C for 3 h.

The Cu/γ-Al₂O₃, Fe/γ-Al₂O₃, Cu/SBA-15 and Fe/SBA-15 samples were used as reference catalysts. Transition metals were deposited by an impregnation method using aqueous solutions of suitable metal nitrates. Detailed description of the synthesis of SBA-15 support and deposition of transition metals was presented in our previous paper [9].

2.2. Catalysts characterization

Chemical compositions of the samples were determined by electron microprobe analysis performed on a JEOL JXA 733 superprobe (electron probe microanalysis – EPMA).

The X-ray diffraction patterns of the raw clays as well as their modifications were obtained with a Philips X'Pert APD diffractometer using CuK_α radiation.

Textural parameters of the samples were determined by N₂ sorption at –196 °C using an ASAP 2010 (Micromeritics) automated gas adsorption system. Prior to the analysis, the samples were outgassed under vacuum at 200 °C for 16 h. The surface area was determined using the BET and Langmuir models, micropore volume of the samples was calculated using the t-method of DeBoer, while distribution of mesopores was determined using the BJH model. Additionally, distribution of micropores was determined from results of Ar sorption at –196 °C using the Horvath–Kawazoe (H–K) model. Micropore size distribution was determined from adsorption branch of isotherm, while desorption branch was used for the determination of mesopore size distribution.

The UV–vis–DRS spectra of the samples were recorded using an Evolution 600 (Thermo) spectrophotometer. The measurements have been performed in the range of 200–900 nm with a resolution of 2 nm.

The surface acidity of the clay materials was studied by adsorption of pyridine, followed by IR spectroscopy. Transmission IR spectra were recorded using wafers in the form of self-supporting pellets of the catalyst powder (ca. 10 mg/cm²). The pellet was placed in a IR cell designed to carry out spectroscopic measurements at different temperatures and equipped with ZnSe windows. The cell was connected to a vacuum line allowing all thermal treatments and adsorption–desorption experiments to be carried out in situ. Prior to pyridine adsorption, the sample was outgassed at 480 °C under vacuum for 1 h. Then the cell was cooled to 170 °C and the catalyst was allowed to react with pyridine for 10 min, subsequently weakly adsorbed pyridine was evacuated for 20 min under vacuum. FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer for the samples outgassed at 170, 250, 350 and 450 °C. 100 scans were taken with a resolution of 2 cm^{−1}.

2.3. Catalytic tests

The modified PCH samples were studied as catalysts for selective reduction of NO with ammonia (NO-SCR, DeNOx). The catalytic experiments were performed in a fixed-bed flow reactor system. The reactant concentrations were continuously measured using a quadrupole mass spectrometer (VG QUARTZ) connected directly to the reactor outlet. Prior to the reaction, each sample (100 mg) of the catalyst was outgassed in a flow of pure helium at 550 °C for 30 min. The following composition of the gas mixture was used: [NO] = [NH₃] = 0.25%, [O₂] = 2.5%. Helium was used as a balancing gas at a total flow rate of 40 ml/min.

The influence of H₂O on the NO-SCR reaction was studied by a periodical addition of water vapor into the reaction mixture. The gas supplying system consisted of two separated helium lines (with pure helium and with He constantly flowing through the saturator kept at 32 °C). The water vapor concentration in the reaction mixture was measured to be about 5.0 vol.%. Helium (used as a balance gas) was switched by means of a 4-port valve from dry to wet in intervals of 30 min. All the gas lines were heated in order to prevent condensation of water.

The influence of SO₂ on the catalytic performance of the studied samples was determined by the following experiment. The catalytic test was performed in isothermal conditions for 1 h. Then a flow of the reaction mixture was exchanged for the flow of SO₂ (2000 ppm) diluted in helium (20 ml/min). The catalyst was kept in the flow of this mixture for 30 min and then the flow of SO₂-containing gas mixture was exchanged for the flow of the reaction mixture. Comparison of the NO conversion and selectivity to N₂ before and after the treatment of the catalyst with SO₂ allowed evaluating its resistance to the poisoning by sulphur dioxide.

3. Results

The chemical composition of the parent clays as well as the PCH materials produced from these clays is presented in Table 1. For vermiculite, additionally the results of chemical analysis for the sample pre-treated with nitric and oxalic acids (acid-Verm) are presented. Silica is a main component of the parent clays and its content increased in the PCH samples. Additionally, aluminium, magnesium and iron, which apart from silica are the components of the clay layers, were found. Lower contribution of sodium, potassium and calcium, which are typically located in the interlayer space of the clays, was measured. The presence of Ti cations was also detected in vermiculite and montmorillonite.

Table 1

Chemical analysis of parent clays and PCH samples.

Sample	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	TiO ₂	K ₂ O	Na ₂ O	CaO
Saponite	56.04	5.64	35.71	0.00	0.00	0.00	2.61	0.00
PCH-Sap	84.06	3.76	11.78	0.00	0.00	0.00	0.40	0.00
Montmorillonite	69.15	21.91	1.60	3.03	0.11	1.03	2.37	0.80
PCH-Mont	80.82	14.30	1.05	1.92	0.08	0.63	0.59	0.46
Vermiculite	45.47	11.08	21.24	13.72	1.90	6.58	0.00	0.00
Acid-Verm	61.45	7.42	11.25	13.48	2.29	4.09	0.00	0.00
PCH-Verm	79.78	3.99	5.82	7.52	1.72	0.79	0.36	0.00

Fig. 1 presents X-ray diffractograms recorded for the parent clays (Na-forms of saponite and montmorillonite and acidic form of vermiculite) as well as calcined and non-calcined PCHs. For the sodium forms of saponite and montmorillonite the diffraction peaks d_{001} attributed to the ordering of the clay layers are present in the positions related to the basal spacing of 1.28 and 1.26 nm, respectively. Diffractogram recorded for acid treated vermiculite contains two peaks characteristic for basal spacing of 1.48 and 1.15 nm. Therefore, this material exhibits two characteristic interlayer distances probably due to various cations located into its interlayer space. The deposition of surfactants and co-surfactants as well as the formation of the silica pillars in the interlayer space of the clays resulted in a shift of d_{001} peaks in direction of the lower values of 2θ angles. This effect is related to an increase of the interlayer distance in the clay materials. These X-ray maxima are broad and centred at the basal spacing of 3.37, 3.74 and 3.45 nm, respectively for the samples obtained from saponite, montmorillonite and vermiculite. For vermiculite, additional peaks related to the basal spacing of 1.75 and 1.00 nm were found. The former peak is probably related to small aggregates of surfactants and co-surfactants located in the interlayer space of the clay, while the last one could be attributed to the stick-together clay layers (not separated by the interlayer space). After calcination the intensity of the main d_{001} peaks decreased (PCH-Sap, PCH-Mont) or this peak disappeared (PCH-Verm). This effect is related to the formation of the delaminated structure, which is characterized by non-parallel ordering of the clay layers.

Textural parameters of the PCH samples are compared in Table 2, while the adsorption–desorption isotherms for PCHs and the parent clays as well as H–K and BJH pore size distributions are presented in Fig. 2(A) and (B), respectively. A gradual increase in nitrogen sorption observed at low to medium partial pressure ($p/p_0 < 0.3$) suggests the presence of supermicropores and small mesopores. An increase in adsorbed volume observed at higher partial pressures could be related to larger mesopores. The hysteresis loops could be qualified to H4 type, corresponding to slit-like pores [10]. The PCH samples are characterized by the presence of both micro- and mesopores (Fig. 2(B)). In the micropore range the broad maxima of pore size distribution were found in the range of 1.02–1.10 nm, while the maxima of mesopore size distribution were present in the range of 2.66–3.17 nm. In Table 2 the surface areas determine according to the BET and Langmuir models are presented. The BET model is related to the multilayer adsorption, while the Langmuir model is based on the monolayer adsorption of adsorbate. Therefore, the former model is more useful for mesoporous materials, where multilayer adsorption is expected, in contradiction to microporous materials, where the Langmuir model is more realistic. Because, the PCH samples contain both micro- and mesopores, the surface areas determined using both these models were presented.

The transformation of the parent clays into PCHs resulted in a dramatic increase of their surface area. The BET surface area of saponite increased from about 60 to 903 m²/g. For montmorillonite

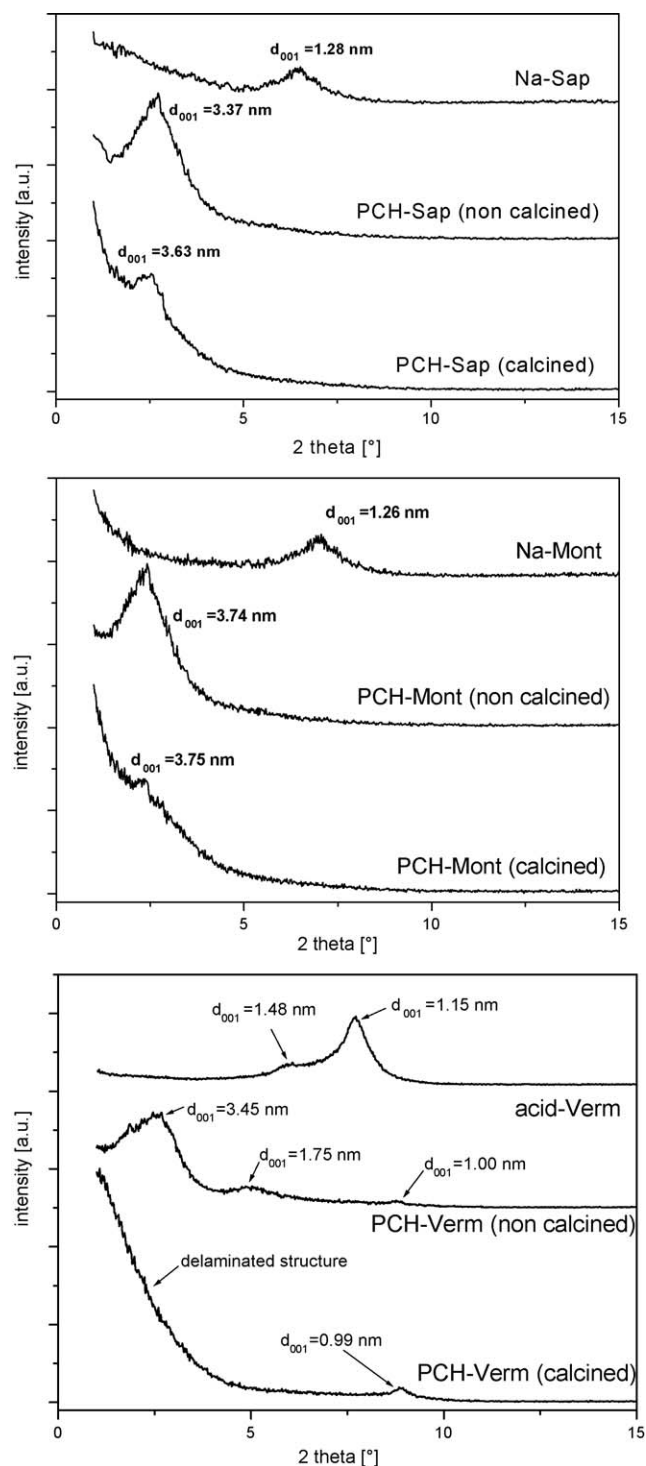


Fig. 1. X-ray diffractograms recorded for parent clays as well as non-calcined and calcined PCHs.

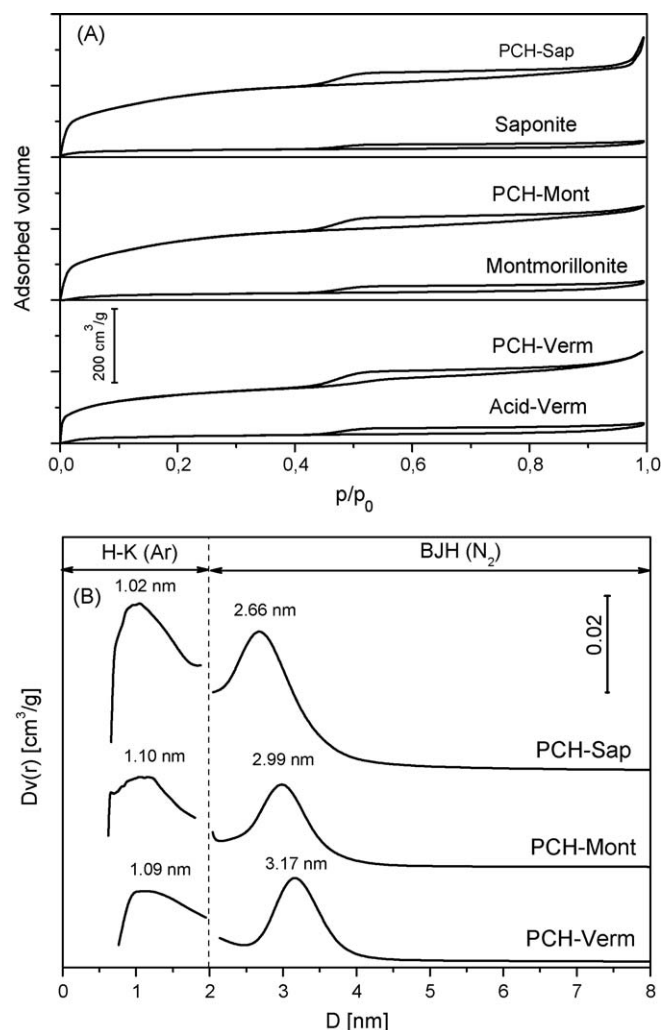


Fig. 2. Nitrogen adsorption–desorption isotherms (A) as well as H–K(Ar) and BJH (N₂) pore size distribution (B) of the PCH materials.

this parameter increased from 77 to 816 m²/g, while for vermiculite from 73 m²/g (measured for the acid treated clay) to 612 m²/g. The surface area measured for the PCH-Verm sample is significantly lower than those determined for other PCHs. This result is in agreement with the XRD data obtained for this material, which has shown that part of the vermiculite layers was not pillared with silica.

The UV–vis–DR spectra recorded for the PCH materials are presented in Fig. 3. No bands were found for the PCH-Sap sample. The broad adsorption peaks were detected in the range of 200–450 nm for PCH-Mont and PCH-Verm. These samples, in contradiction to PCH-Sap, contain significant amount of iron and titanium. The UV–vis–DR spectra of the iron containing samples are characterized by the bands related to Fe³⁺ ← O charge transfer. The position of this band depends on coordination and agglomeration of iron species [11,12]. Mononuclear Fe³⁺ cations give rise

Table 2
Textural parameters of the PCH samples.

Sample	Parent clay	S_{BET} (m ² /g)	S_{mezo} (m ² /g)	S_{Langmuir} (m ² /g)	V_{total} (cm ³ /g)	V_{micro} (cm ³ /g)
PCH-Sap	synthetic saponite	906	104	1250	0.743	0.602
PCH-Mont	natural montmorillonite	816	380	1095	0.542	0.297
PCH-Verm	natural vermiculite	612	288	865	0.401	0.221

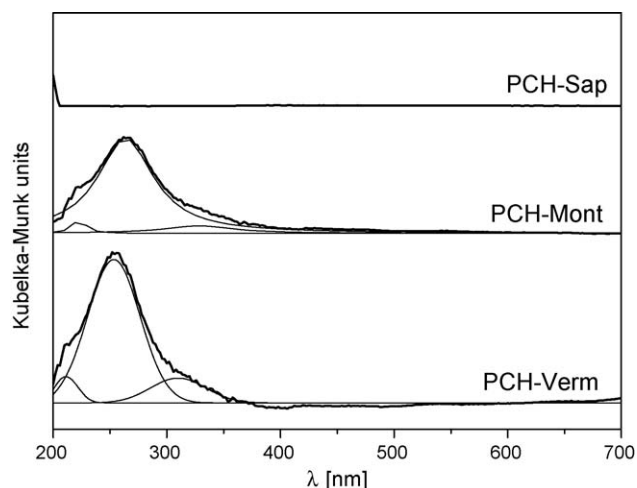


Fig. 3. UV-vis-DR spectra recorded for the PCH samples.

to bands in the range of 200–300 nm. The bands in the region of 300–400 nm are characteristic for small oligonuclear Fe_xO_y clusters, while bulky particles of Fe_2O_3 gives characteristic bands above 400 nm [13]. Additionally, in the case of isolated Fe^{3+} cations distinguishing between iron ions in the tetrahedral (band below 250 nm) and octahedral (band in the range of 250–300 nm) coordination is possible [11,12]. The spectra recorded for PCH-Mont as well as PCH-Verm were deconvoluted into three sub-bands. In both cases the sub-band centred in the range 250–300 nm dominated. Therefore, majority of isolated Fe^{3+} cations is located in the octahedral positions of the clay layers. Only small bands were found for mononuclear iron ions in the tetrahedral coordination as well as for small oligonuclear Fe_xO_y clusters. It should be noticed that the PCH-Verm sample, apart from iron, contained also significant amount of titanium. Isolated Ti^{4+} cations give characteristic bands at about 200 nm and 260 nm, for ions in the tetrahedral and octahedral coordination, respectively. Anatase clusters are characterized by the band situated at about 330 nm [14]. Therefore, overlapping of the bands related to the presence of iron and titanium species cannot be excluded.

Transition metals (Cu, Fe) were deposited on the surface of the PCH materials using an ion-exchange method. Table 3 summarizes the BET surface area and the content of transition metals present in the samples. The deposition of copper and iron only slightly limited the surface area of PCHs. Nearly the same loading of copper and iron was found for saponite based PCH, while significant differences in the content of these metals were detected for PCHs obtained from montmorillonite and vermiculite. However, it should be noted that both parent vermiculite and montmorillonite contain large amount of iron, which is a natural impurity of these minerals. Therefore, also PCHs obtained from these clays exhibited significant content of iron (cf. Table 1). As it was showed above, iron in PCHs not modified with transition metals is located mainly

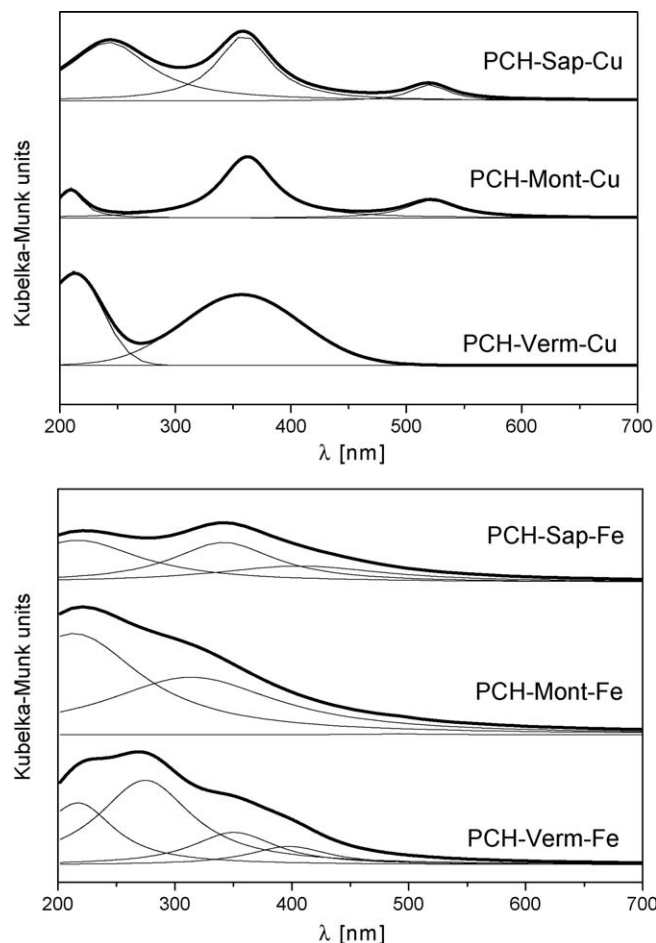


Fig. 4. UV-vis-DR spectra of the PCH samples modified with iron and copper.

in the octahedral sub-layers of the clays. Fig. 6 shows the UV-vis-DR spectra of the samples modified with copper and iron. It should be mentioned that these spectra are the results of the subtraction of the original spectra recorded for the PCH support from the original spectra of this support modified with transition metal, therefore, the spectra presented in Fig. 4 are related only to the deposited transition metals.

The spectra recorded for the Cu-containing samples consist of three maxima centred at about 220–240, 360 and 530 nm. The first peak is attributed to the charge-transfer between mononuclear Cu^{2+} ion and oxygen. The maximum at about 360 nm can be ascribed to the charge-transfer between Cu^{2+} and oxygen in oligonuclear $[\text{Cu}-\text{O}-\text{Cu}]_n$ species [15], while the peak at about 530 nm, present only in the spectra recorded for PCH-Sap-Cu and PCH-Mont-Cu, is related to the d–d transition of Cu with an octahedral environment in CuO [15]. It could be concluded that in a series of the Cu-modified samples, copper is present mainly in the

Table 3

BET surface area and transition metal (TM) loading of PCHs.

Sample	S_{BET} (m^2/g)	S_{meso} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	TM loading [wt. %]
PCH-Sap-Cu	832	98	0.696	0.563	1.41 (Cu)
PCH-Sap-Fe	840	101	0.702	0.560	1.43 (Fe)
PCH-Mont-Cu	782	364	0.512	0.279	1.23 (Cu)
PCH-Mont-Fe	754	358	0.488	0.272	5.56 (Fe)
PCH-Verm-Cu	588	272	0.383	0.203	1.61 (Cu)
PCH-Verm-Fe	565	266	0.372	0.189	10.35 (Fe)

form of isolated cations and oligomeric $[\text{Cu}-\text{O}-\text{Cu}]_n$ species. In the case of PCH-Sap-Cu and PCH-Mont-Cu, also bulky CuO clusters were found.

The spectra obtained for the Fe-modified samples were deconvoluted into few bands. The peaks centred at about 220–230 nm are related to the presence of isolated Fe^{3+} cations in the tetrahedral coordination, while the band at about 270 nm is attributed to the presence of mononuclear Fe^{3+} ions in the octahedral coordination [11–13]. The range of 300–400 nm is characteristic of the bands assigned to small Fe_xO_y clusters [16], while in the region above 400 nm the bands related to the presence of bulky Fe_2O_3 clusters can be found [17]. The analysis of the UV–vis-DR spectra showed that iron deposited in PCHs was present mainly in the form of isolated cations and small oligomeric Fe_xO_y clusters.

The surface acidity of PCHs was determined by the adsorption of pyridine, followed by IR spectroscopy. The number of acidic sites (both Brønsted and Lewis) was calculated from the intensities of the IR band, characteristic of pyridinium ions (band at 1545 cm^{-1}) as well as coordinatively bonded pyridine (band at 1450 cm^{-1}) and respective absorption coefficients, 0.078 and $0.165\text{ cm}^2/\mu\text{mol}$ [18,19]. Thermodesorption of pyridine was performed to estimate the relative strength of acidic centres in all the examined samples. An example of spectra recorded after pyridine sorption and consequent thermodesorption for the PCH-Sap sample is presented in Fig. 4 while the concentration of pyridine adsorbed on Lewis and Brønsted acid sites is shown in Fig. 5. It should be noted that among the studied PCH materials, the highest surface acidity was presented by the sample obtained from montmorillonite. Lower concentration of acid sites was found for the PCH-Verm sample, while the lowest acid strength presented PCH produced from synthetic saponite. Lewis type acid sites dominated over Brønsted in case of all the studied materials. At desorption temperature as high as 450°C , the band related to pyridine adsorbed on Lewis acid sites was found only for PCH-Mont. Therefore, it could be concluded that this sample is characterized, not only by the highest concentration of surface acid sites, but also by the strongest acid sites.

The deposition of copper on PCHs significantly increased the surface concentration of Lewis acid sites and reduced the number of Brønsted acid centres (cf. Figs. 6 and 7(A)). The highest surface acidity, practically related only to Lewis acid sites, was measured for the montmorillonite-based sample. Lower acidity was found in

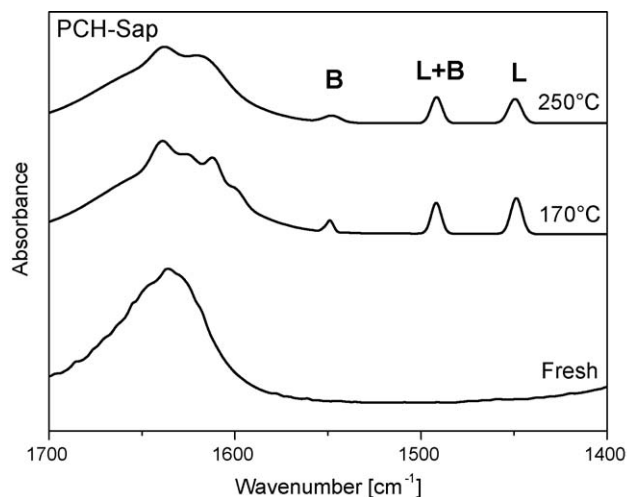


Fig. 5. FT-IR spectra of pyridine adsorbed and desorbed at increasing temperatures on PCH-Sap: L – Lewis-type acid sites, B – Brønsted-type acid sites.

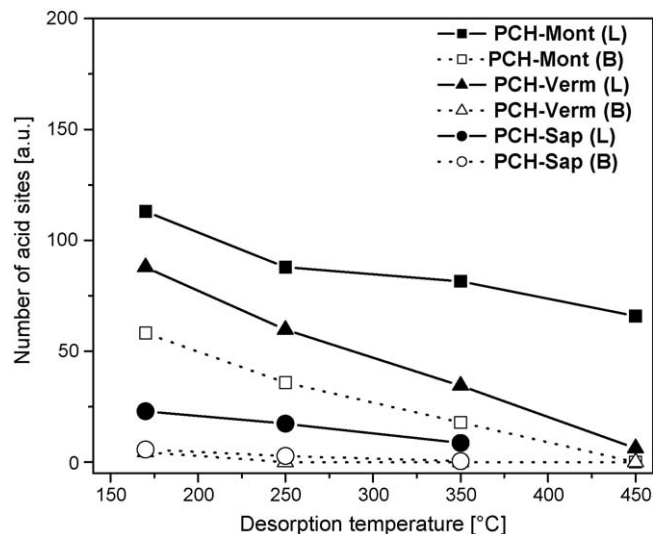


Fig. 6. Surface acidity of the PCH sample: L – Lewis-type acid sites, B – Brønsted-type acid sites.

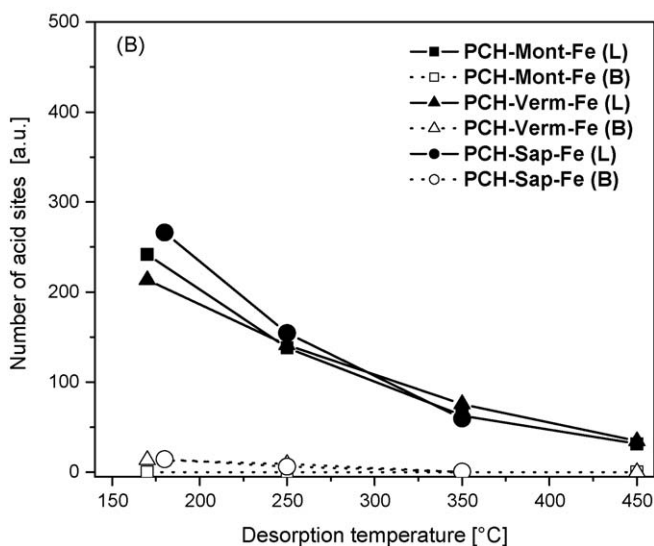
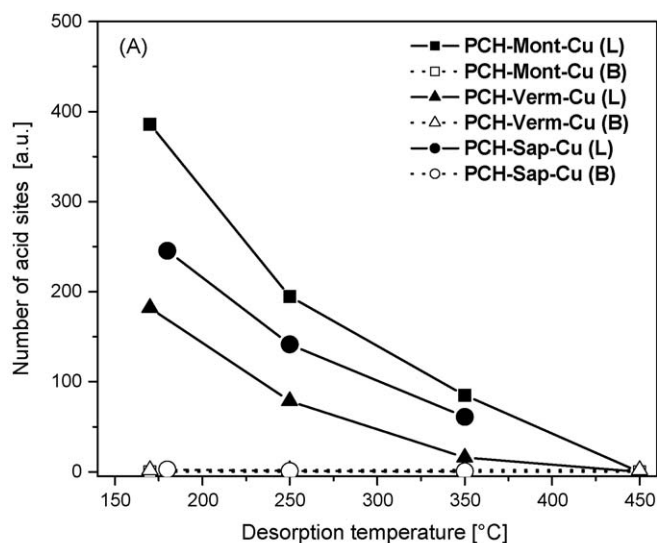


Fig. 7. Surface acidity of PCHs modified with copper (A) and iron (B): L – Lewis-type acid sites, B – Brønsted-type acid sites.

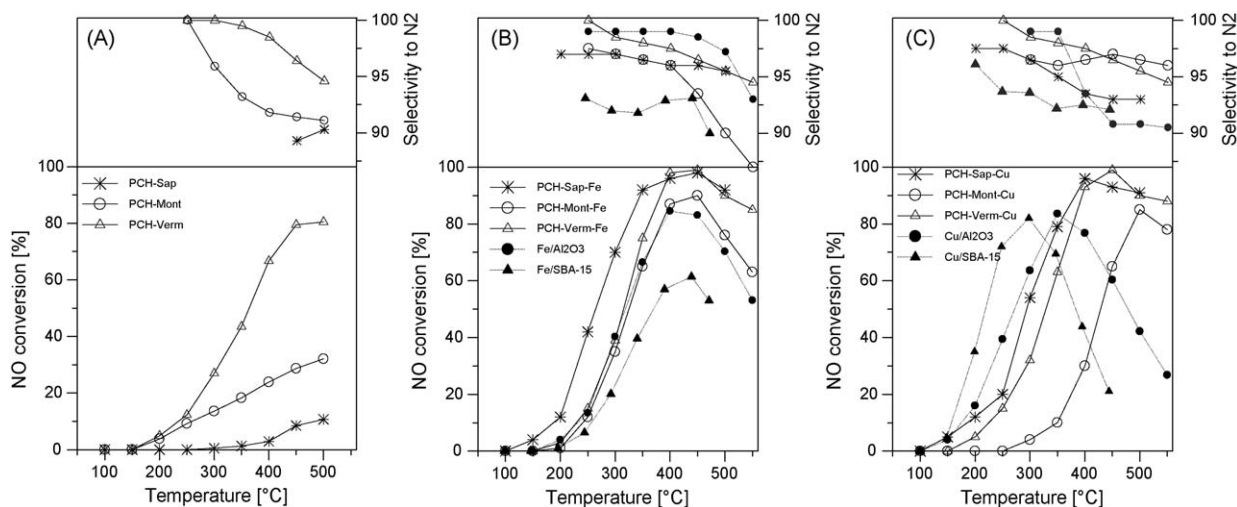


Fig. 8. Results of catalytic tests for the PCH supports (A) and samples modified with iron (B) and copper (C).

PCH produced from saponite, while the samples obtained from montmorillonite showed the lowest surface acidity.

A series of the Fe-modified samples has shown a very similar surface acidity related mainly to the presence of Lewis acid sites (Fig. 7(B)). It should be noted that at temperature as high as 450 °C pyridine molecules adsorbed on Lewis acid sites were still detected. Therefore, it seems that the deposition of iron, besides of weak and medium acid centers, generated also small amount of very strong acid sites.

The PCH samples were tested in the role catalysts for selective catalytic reduction of NO with ammonia (NO-SCR, DeNOx). Nitrogen and water vapour are desired products of this process, while N₂O is undesired side-product. The results of the studies performed for PCHs not modified with transition metals are presented in Fig. 8(A). Among these samples, the best results were obtained for vermiculite based PCH (PCH-Verm). The NO conversion exceeded 80% with the selectivity to N₂ above 94% at temperature higher than 450 °C. Therefore, this material seems to be a very interesting candidate for the high-temperature NO-SCR catalyst. It is worthy to mention that the synthesis of this catalyst is much cheaper, easier and faster than the other studied catalysts because the preparation procedure does not include the step of the deposition of active component.

The deposition of iron on PCHs significantly increased their catalytic activity in the NO-SCR process. The best catalytic results were found for PCH-Sap-Fe (Fig. 8(B)). The NO conversion at the level higher than 90% was obtained in the range of 350–500 °C. What is important the activity of this catalyst is significantly higher than PCH-Verm (Fig. 8(A)). Therefore, it seems that iron species deposited on the PCH walls are significantly more active than iron cations incorporated into the clay layers. The lower activity was presented by PCH-Verm, while the PCH-Mont sample was the least active in a series of the PCH based samples. The reference catalysts (Fe/Al₂O₃ and Fe/SBA-15) presented significantly lower catalytic activity in the DeNOx process than PCHs modified with iron. For all the catalyst competitive ammonia oxidation by oxygen decreased the NO conversion at temperatures higher than 450 °C. A decrease in the selectivity to N₂ observed for PCH-Mont-Fe, Fe/SBA-15 and Fe/Al₂O₃ at higher temperatures suggests that part of ammonia was oxidised to N₂O. Probably, this side process is also responsible for a very small efficiency of the Fe/SBA-15 catalyst in the high temperature region.

In a series of the Cu-modified samples, similar activity was found for the samples obtained from saponite and vermiculite

(Fig. 8(C)). In a group of the clay based sample, PCH-Sap-Cu was more active at lower temperatures ($T < 400$ °C), while the PCH-Verm-Cu catalyst showed higher activity at temperatures above 400 °C. For both the catalysts, the NO conversions above 90% in the range of 400–500 °C were obtained. The PCH-Mont-Cu sample presented the lowest catalytic activity in a series of the PCH samples. Competitive ammonia oxidation significantly reduced the effectiveness of NO reduction in the high temperature region. The reference catalysts (Cu/Al₂O₃ and Cu/SBA-15) were found to be more active at lower temperatures, however their effectiveness in the DeNOx process was significantly limited in the high temperature range due to the competitive reaction of ammonia oxidation.

The temperatures needed for 50% of the NO conversion as well as the selectivity to N₂ measured at these temperatures are comparatively presented in Fig. 9. The NO conversion has not reached the level of 50% for the PCH-Mont and PCH-Sap catalysts in the whole studied temperature range and therefore these samples were not included in this figure. Both, in a series of the Fe- as well as Cu-containing catalysts, 50% of the NO conversion was possible at the lowest temperatures for the SBA-15 based samples. However, it should be also noted that these catalyst presented rather poor activity in the high temperature range.

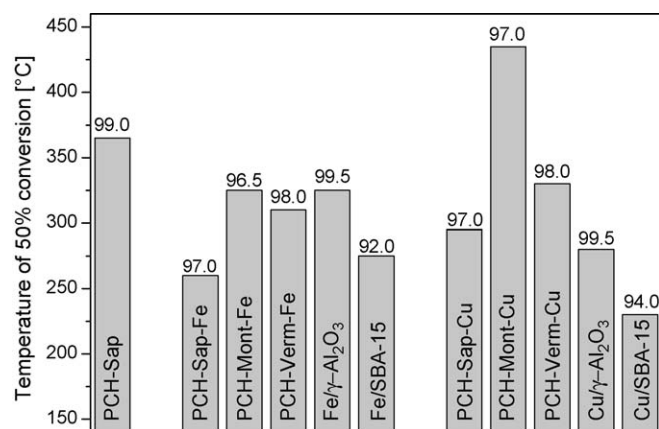


Fig. 9. Comparison of the catalytic performance of the studied samples in the DeNOx process: bars- temperatures needed for 50% of NO conversion; numbers above bars -selectivity to N₂ at these temperatures.

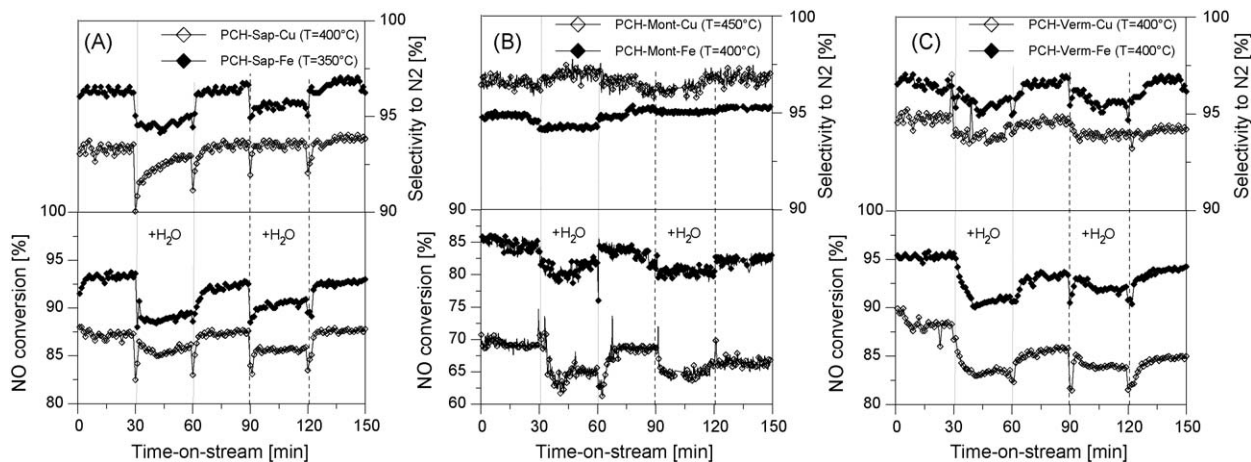


Fig. 10. Study of influence of water vapour on catalytic activity of PCH-Sap(A), PCH-Mont (B) and PCH-Verm (C) modified with copper and iron.

Water vapour and sulphur dioxide are typical components of outlet gases emitted by electric power stations and may cause deactivation of the DeNO_x catalysts. The influence of water vapour on the catalytic activity of the PCH samples was studied by a periodical addition of steam into the reaction mixture. The results of these isothermal tests are presented in Fig. 10. An addition of water vapour (~5.0 vol.%) into reaction mixture resulted in a decrease of the NO conversion and, for majority of the samples, also the selectivity to nitrogen. The activity of PCH-Sap-Cu was the least affected by the presence of steam. In this case the NO conversion decreased only by about 2%, while the selectivity to N₂ dropped from 94% to about 92.5% at temperature 350 °C. The strongest deactivation of the catalyst, which decreased the NO conversion by about 5.5%, was observed for PCH-Verm-Cu.

Fig. 11 presents the results of the studies of influence of SO₂ on the catalytic performance of the PCH-based catalysts. The activity and selectivity of the Cu-containing samples was not affected or only slightly affected by SO₂. Both parameters were nearly the same before and after treatment of the catalysts with SO₂. The Fe-modified PCH samples were found to be less resistant for the poisoning by sulphur dioxide. The highest deactivation effect was observed for PCH-Sap-Fe, where the NO conversion decreased by about 2%. For other catalysts of this series, the activity was only slightly affected by SO₂ treatment.

4. Discussion

4.1. Structure and composition of the clay samples

All the parent materials, which were included in these studies belong to a group of the layered cationic clays. The layer of saponite consists of the octahedral magnesia sublayer sandwiched between two tetrahedral silica sublayers. Therefore, MgO and SiO₂ are the main two components of this clay. Part of Si⁴⁺ cations in the tetrahedral sheet is substituted by aluminium ions. Sodium cations, which are located in the interlayer space of saponite, compensate the negative charge of the clay layers. The interlayer distance determined by XRD measurements suggest that these cations are present in the hydrated form. Montmorillonite consists of the alumina-silica layers. The octahedral alumina sublayer is located between two tetrahedral silica sublayers. Part of aluminium cations in the octahedral sublayer is substituted by Mg²⁺ ions, while Na⁺, K⁺ and Ca²⁺ cations are located in the interlayer space of montmorillonite and compensate the negative charge of the clay layers. The vermiculite layers consist of three sublayers. The octahedral magnesia sublayer is sandwiched between two tetrahedral silica sheets. Part of Mg²⁺ cations in the tetrahedral sublayer is substituted by Al³⁺ ions. The negative charge of the clay layers is compensated by interlayer potassium and magnesium cations.

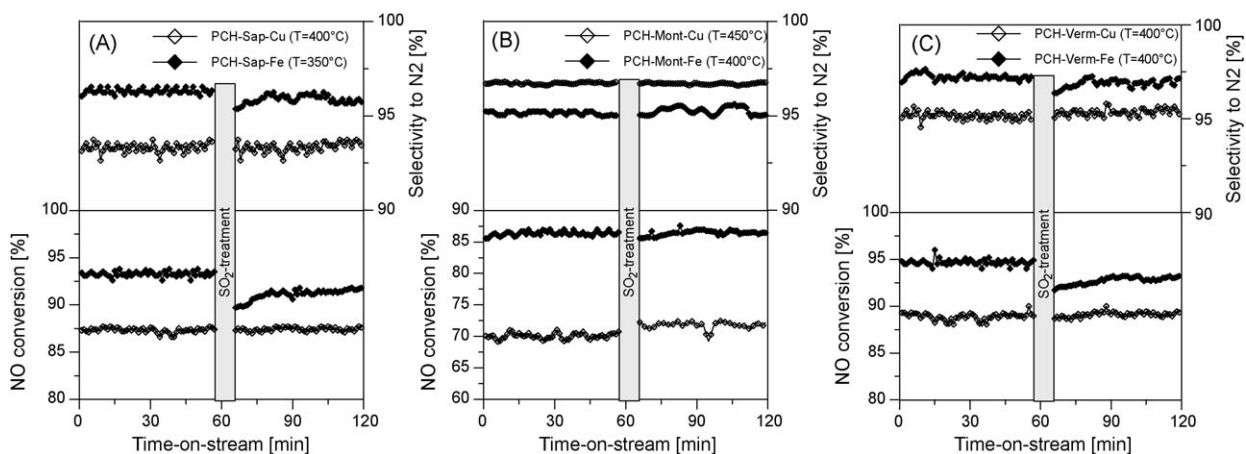


Fig. 11. Study of influence of SO₂ on catalytic activity of PCH-Sap (A), PCH-Mont (B) and PCH-Verm (C) modified with copper and iron.

It should be noted that the content of interlayer cations in the parent clays was significantly higher than in the PCH materials (Table 1). This effect is related to the partial exchange of these cations by the molecules of ionic surfactant (hexadecyltrimethylammonium ions), which is one of the stages of the PCH synthesis.

It should be noted that vermiculite contains larger concentration of iron than montmorillonite. Iron, as was shown by UV–vis-DRS analysis, is located mainly in the octahedral layers of montmorillonite and vermiculite. Additionally, small contribution of iron in tetrahedral positions of the clay layers and in the form of small oligomeric iron oxides species was detected. These results are in agreement with data presented in literature, which shows that part of aluminium (in montmorillonites) or magnesium (in vermiculites) in octahedral position could be substituted by iron cations [20]. Acid pre-treatment of vermiculite resulted in leaching of significant amounts of aluminium from the tetrahedral sublayers and additionally decreased the content of Mg^{2+} and K^+ cations (Table 1). Part of interlayer cations was exchanged for protons during the acid pre-treatment of the clay, however in the case of magnesium, partial leaching of these cations from the clay layers cannot be also excluded. An additional decrease in content of these cations was observed for the PCH sample (PCH-Verm) due to their partial exchange for hexadecyltrimethylammonium ions.

The basal spacing of the layered clay minerals depends on the thickness of the clay layer and interlayer distance. The thickness of the clay layers is estimated to be about 0.96–1.00 nm [21]. The interlayer distance depends on the type of interlayer cations, their arrangement and the degree of their hydration. Kawano and Tomita [22] have reported that the basal spacing for totally dehydrated saponite in the sodium form is 0.98 nm, while for the hydrated clay the basal spacing increased to 1.28 nm. Therefore, it could be concluded that saponite used in our studies contains hydrated sodium cations in the interlayer space. According to the chemical analysis (Table 1), montmorillonite contains interlayer sodium, potassium and calcium cations. The basal spacing in the potassium-form of the clay may change in the range of 1.01–1.24 nm, respectively for dehydrated and the hydrated clay. In the case of the Ca-form of clay the basal spacing for dehydrated material is about 0.97 nm and such material is much more resistant for hydration than the sodium and potassium forms of the clays [22]. Therefore, the basal spacing determined for studied montmorillonite (Fig. 1) is similar to the values characteristic for the clay containing hydrated sodium and potassium cations in the interlayer space. Two peaks related to the basal spacings of 1.15 and 1.48 nm were found for vermiculite pre-treated with acids. The chemical analysis of vermiculite has shown the significant content of potassium and magnesium, which are probably present in the form of interlayer cations (Mg^{2+} is also component of the clay layers). Kawano and Tomita [21] have shown that the basal spacing of the K- and Mg-forms of vermiculite is 1.03 and 1.48 nm, respectively. Probably the former value is related to the presence of dehydrated cations, while the last one to hydrated cations. The shift of 001 reflexes in direction of lower values confirm successful pillaring of saponite montmorillonite and vermiculite (Fig. 1). However, the significant broadening of these peaks may suggest partial disordering of the clay layer arrangement. For non-calcined PCH-verm additional peaks related to not pillared or even stick together clay layer layers were found. The later effect is possible when protons (during the acids pre-treatment of vermiculite) migrated from the interlayer space into the clay layers resulting in the neutralization of the negative charge of the layer [6]. The XRD studies have shown that the calcination of the PCH samples resulted in a significant disordering of the clay layer arrangement and formation the delaminated structures.

4.2. Catalytic performance of PCHs

Surface acidity of the DeNOx catalysts is a very important factor influencing their activity and selectivity. For majority of the DeNOx catalysts Eley–Rideal mechanism including reaction between chemisorbed ammonia molecule and NO (in gas phase or weakly adsorbed) was suggested [23]. Ammonia molecules are chemisorbed and activated on acid sites. Therefore, study of the concentration, strength as well as chemical nature of acid sites are very important. Both Brønsted and Lewis acid sites were found in the PCH samples. The $\equiv Si-OH-Al \equiv$ bridges, being Brønsted acid sites, can be situated in different locations, depending on the type of the clay and their modification. Such bridges are present in the saponite and vermiculite tetrahedral sublayers. In the case of montmorillonites such $\equiv Si-OH-Al \equiv$ bridges are responsible for bonding the octahedral alumina sublayer and tetrahedral silica sheet. Therefore, in the last case such Brønsted acid sites can be exposed only on the edges of the montmorillonite crystallites, while for PCHs obtained from saponite and vermiculite such centres should be located on the surface of the clay layers. Lewis acid sites exist in PCH due to the presence of aluminium in the tetrahedral sheet of saponite and vermiculite as well as octahedral sublayer of montmorillonite. Probably, the presence of transition metal cations (Fe^{3+} , Fe^{2+} , Ti^{4+}) incorporated into the clay structure also generated the Lewis-type acidity.

The deposition of copper or iron on PCHs significantly increased the surface concentration of Lewis acid sites and reduced the number of Brønsted acid centres. This effect is related to the exchange of protons compensating the negative charge of the clay layers for copper cations.

Among PCHs not modified with transition metals, the vermiculite based sample presented significantly higher catalytic activity in the process of selective reduction of NO with ammonia than the catalyst obtained from montmorillonite. PCH produced from saponite showed the lowest activity. This activity order well correlates with the content of iron, which is a natural component of the parent vermiculite and montmorillonite (cf. Table 1) and is also known to be a catalytically active component of the NO-SCR catalysts (e.g. [24,9,25]). The UV–vis-DRS measurements performed for the PCH samples have shown that iron is located mainly in the octahedral sub-layer, which is sandwiched between two tetrahedral sheets of the clay. Therefore, only iron cations located at the edges of the clay layers are available for the reacting molecules. Additionally, the influence of titanium, which was found to be a natural impurity of studied vermiculite and is a typical component of the commercial DeNOx catalysts (e.g. [26,27]), on the catalytic performance of PCH-Verm cannot be excluded. Lower catalytic activity was presented by the PCH sample produced from montmorillonite. This material contains significantly lower content of iron (Table 1), which is also located in the octahedral sheets of the clay layers. The lowest activity was measured for the sample obtained from synthetic saponite, which contain neither iron nor titanium.

The deposition of iron on PCHs significantly increased their catalytic activity in the NO-SCR process. The best catalytic results were found for PCH-Sap-Fe (Fig. 8(B)). What is important the activity of this catalyst is significantly higher than PCH-Verm (Fig. 8(A)). Therefore, it seems that iron species deposited on the PCH walls are significantly more active than iron cations incorporated into the clay layers. The lower activity was presented by PCH-Verm, while the PCH-Mont sample was the least active one. For all the catalyst competitive ammonia oxidation by oxygen decreased the NO conversion at temperatures higher than 450 °C. A decrease in the selectivity to N_2 observed for PCH-Mont-Fe at higher temperatures suggests that part of ammonia was oxidised

to N_2O . The Fe-modified PCH materials are characterized by the similar acidic properties (cf. Fig. 7(B)), therefore it seems that this parameter cannot be responsible for such significant differences in the catalytic performance observed in this series of the samples. PCH-Sap-Fe, which was found to be more active than the other samples of this series, apart from iron present in the form of isolated cations and small oligomeric Fe_xO_y species, contained also bulky Fe_2O_3 clusters. Iron cations in such clusters can be reduced at lower temperatures than isolated Fe^{3+} ions or oligomeric iron oxide species [28,29]. Therefore, it could be expected that bulky iron oxide would be catalytically active at lower temperatures than less aggregated iron species. The PCH-Verm-Fe sample, which was found to be less active than PCH-Sap-Fe, was characterized by lower content of the bulky iron oxide clusters, while such species were not detected for less active PCH-Mont-Fe (cf. Fig. 7). Another explanation of the differences in the catalytic activity within this series of the samples could be a significantly higher surface area of PCH-Sap-Fe comparing to the other catalysts. Probably the higher surface area guaranteed the better dispersion and more uniform distribution of the deposited active component.

In a group of the Cu-modified samples similar activity was presented by the catalysts obtained from saponite and vermiculite (Fig. 8). PCH-Sap-Cu was more active at lower temperatures, while the PCH-Verm-Cu catalyst showed better effectiveness at higher temperatures. Significantly lower activity was found for PCH-Mont-Cu. Probably, the type of copper species deposited on the support surface as well as its acidity influenced the catalytic performance of the Cu-containing samples. The less active PCH-Mont-Cu sample contained significantly smaller contributions of isolated cations than the other more active catalysts (cf. Fig. 4). Therefore, it seems that there is much better distribution of copper deposited on PCH-Sap-Cu and PCH-Verm-Cu comparing to the PCH-Mont-Cu sample. On the other hand, isolated Cu^{2+} cations are reported to be responsible for the activity in high-temperature DeNOx and, in contradiction to the more aggregated copper oxide species, are less active in the side process of ammonia oxidation [9]. PCH-Mont-Cu, which presented the lowest activity in this series of the samples, was characterized by the presence of stronger acid sites than the other more active catalysts. If we assume that the DeNOx process proceeds according to the Eley–Rideal mechanism and includes the reaction between chemisorbed ammonia species and gaseous or weakly bonded NO [27,30–32], it seems possible that strongly chemisorbed ammonia is oxidised not only to N_2 but also much deeper to nitrogen oxides. Such effect was reported by Schneider et al. [33] for Lewis-bonded ammonia species in the absence of NO. Additional studies are needed to solve this interesting problem.

The studied catalysts have been found to operate effectively in the presence of water vapour and SO_2 introduced into the reaction mixture. It should be noted that effect of water vapour addition has not resulted in a permanent deactivation of the catalysts and exchange from wet to dry reaction mixture resulted in a full or partial reactivation of the catalysts. Therefore, it seems that the competition of water and ammonia molecules for the same adsorption sites was responsible for the observed small decrease in the NO conversion.

5. Conclusions

The new method of the PCH synthesis from acid pre-treated vermiculite was proposed. The chemical composition, textural and

structural parameters as well as surface acidity of this material were determined and compared with the parameters of PCHs obtained from natural montmorillonite and synthetic saponite. The PCH samples were tested in the role of the catalysts for selective reduction of NO with ammonia. The best results were obtained for the vermiculite based sample (PCH-Verm). The high catalytic activity of this sample was attributed to high content of iron and titanium, which were natural impurities of vermiculite. The deposition of transition metals (Cu, Fe) on the PCH materials significantly increased their catalytic activity. The best results were obtained for the PCH-Sap-Fe catalyst, which was able to convert more than 90% of NO, with the high selectivity to nitrogen in the temperature range of 350–500 °C. The PCH based catalysts were not deactivated or only slightly deactivated by water vapour and SO_2 .

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